

THE STRUCTURE OF PETROLEUM ASPHALTENES  
AS INDICATED BY PROTON MAGNETIC RESONANCE

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### Introduction

Proton magnetic resonance has been used in the past to provide information on the structure of asphalt fractions. In a paper by R. B. Williams,<sup>1</sup> the proton magnetic resonance data are combined with infrared data to yield information suggesting the size of the clusters of aromatic rings in a number of asphalt fractions, including asphaltenes. Gardner, Hardman, Jones, and Williams<sup>2</sup> used proton magnetic resonance to provide information on the structure of thermal diffusion fractions of petroleums from an asphalt.

In the present study, the proton magnetic resonance data have been combined with other analytical data and contributions from the literature to yield information about the structures of four asphaltenes. The four asphaltenes include two asphaltenes from asphalt crude oils, an asphaltene produced by air blowing, and another produced through a cracking process.

### Proton Magnetic Resonance Data

Proton magnetic resonance spectra were obtained on a Varian Model A-60 NMR spectrometer at 14,090 gauss. The solvent used was carbon disulfide. Spectra used as a basis for quantitative analysis were taken with a sweep width of 1000 cycles per second, a sweep time of 250 seconds, an RF field of 0.08 milligauss, and a filter band width of one cycle per second.

Characteristic spectra for the four asphaltenes are given in Figures 1, 2, 3, and 4. The horizontal scale of the spectra, labeled PPM, shows the "chemical shift" downfield from a reference material, tetramethylsilane, at which the various proton types appear. The magnitude of the shift is expressed in parts per million of the reference field, 14,090 gauss.

The Varian A-60 spectrometer resolves the hydrogens into four classes. These classes are methylene, methyl, benzylic, and aromatic. Aromatic protons are seen at 6.5 to 8 ppm. Benzylic protons appear at 2 to 3 ppm. The methylenic hydrogens give the tall peak at 1.2 ppm, while the methyl protons produce the peak at 0.8 ppm on the shoulder of the methylene peak.

The amplitude of the peaks is governed by the concentration of the particular hydrogen type and also by the instrument settings. Thus, it has no absolute value and the spectra have a purely arbitrary vertical scale. For the purposes of this study, only the intensity of the various peaks relative to that of the methylene peak is required.

Encl.-Tables I and II  
Figures 1 through 8  
(RD 622541, RD 622542,  
RE 622497, RE 622498,  
RD 622499, and RE 622500)

The peaks obtained were compared by planimetry. The repeatability in the area measurement obtained this way was better than 1% in the case of the large peaks. For the smallest peaks, such as that due to the aromatic proton of the asphaltene from the air-blown California residuum, the repeatability was  $\pm 6\%$  to  $8\%$ . The peak from the aromatic proton of the Venezuelan asphaltene was too small to measure. The error in repeatability of the spectra themselves was negligible.

Figure 1 shows the spectrum of an asphaltene from a Venezuelan crude oil which is widely used for asphalt manufacture. Figure 2 is the spectrum of an asphaltene from a crude oil of the San Joaquin Valley Area in California. This oil is also widely used for asphalt manufacture. The spectrum of Figure 3 is that of an asphaltene produced by laboratory air blowing at  $475^{\circ}\text{F}$  of the residuum from the California crude oil of Figure 2. In this process, about 85% of the total asphaltene contained in the air-blown asphalt are formed in the air-blowing process. Figure 4 shows the spectrum of the benzene soluble, heptane insoluble asphaltene produced in cracking the California residuum of Figure 2. This cracking was done by a refinery thermal cracking unit operating at a temperature of  $900^{\circ}\text{F}$ .

Analytical data on these asphaltene are given in Table I. It is recognized that asphaltene are heterogeneous substances and that these data, therefore, refer to the average composition. However, it is not possible to deviate very widely from these analytical results and still have asphalt fractions which retain the solubility characteristics of the asphaltene class.<sup>3</sup>

The areas under the peaks of Figures 1, 2, 3, and 4 were measured for each of the classes of protons to give a quantitative measure of the relative amounts of each type of proton present. The base line for these areas is that of the minimum shown in the spectra between the peaks for the aromatic and benzylic protons.

The areas so obtained were all divided by the area for the methylenic protons in that particular spectrum to provide ratios between the amounts of the different proton classes present. These ratios are given in Table II.

#### Average Molecular Structures

Using the ratios between the four classes of hydrogens and other chemical and physical data, one can construct formulas which are consistent with these data. This has been done to provide the average molecular structures of Figures 5, 6, 7, and 8. The ratios between the hydrogen types shown on the figures are those of the molecular structures drawn. They fit as closely as was possible the data of Table II on the asphaltene.

A brief justification for the drawing of average asphaltene molecules may be desired at this point. It is recognized that asphaltene are a heterogeneous classification and that the possibilities for variation from molecule to molecule are almost infinite. Also, the average structure of various fractions from asphaltene will differ. Nevertheless, there is an over-all average ring size, an average content of polar atoms, and some arrangements which are preferred over others. For the very reason that the individual molecules are different, we are forced to consider average structures. We believe that these are sufficiently helpful in giving a general idea of the nature of the species to overcome the criticism that they are only average structures.

Among the pertinent literature which is drawn upon to arrive at the structures portrayed may be cited the high mass spectrograph data of Clerc and O'Neal<sup>4</sup> on

asphalt, wherein polynuclear aromatic ring systems were identified and also the work of Carlson and O'Neal<sup>5</sup> on heavy petroleum compounds wherein it was deduced that the rings in these compounds were condensed together and that the aliphatic portion of the molecule was primarily one long chain. Sergienko and Pustil'nikova<sup>6</sup> and Fischer and Schramm<sup>7</sup> have conducted hydrogenation experiments on asphalts leading to the conclusion that sulfur and oxygen compounds form the majority of the connecting links between segments of the asphaltene molecules. Goppel and Knotnerus<sup>8</sup> deduced from chemical analyses that three fifths of the bonds formed in the air-blowing process were ester bonds. Evidence that the nitrogen in asphaltenes is primarily included in the condensed ring portion of the molecule was provided by the studies of Ball, et al.<sup>9</sup> Additional evidence regarding the types of oxygen containing functional groups was provided by Knotnerus.<sup>10</sup> X-ray diffraction studies by Erdman and coworkers<sup>11</sup> indicated that the asphaltenes consisted of systems of polynuclear aromatic plates carrying side chains and connecting links of paraffinic nature. The size of the condensed ring systems in the molecules of Figures 5 through 8 is consistent with Erdman's X-ray diffraction data.<sup>11</sup>

The molecular weights of the asphaltenes of this study were not determined. They are assumed to fall in the range between 2000 and 3000 molecular weight which is indicated by recent research<sup>12,6,7,13</sup> on asphaltene molecular weights. In systems where association of the asphaltenes can occur, extremely high molecular weights, up to 500,000, can be obtained.<sup>12</sup> However, where conditions of the determination are such as will minimize asphaltene association, the values appear to fall in the vicinity of 2000 to 3000.<sup>6,7,13</sup> A lower molecular weight is assumed for the cracked tar asphaltene, as it is derived by degradation of natural asphaltenes with breaking off of side chains and aliphatic connecting links between ring systems.

The air-blown asphaltene of Figure 7 is purposely shown less condensed than the natural asphaltenes (Figure 5) as the air-blown asphaltenes are made by condensation and aromatization of the smaller and less polar resin molecules. The natural asphaltenes may also polymerize; however, in the air-blown California residuum the bulk of the asphaltenes come from nonasphaltene precursors. Ester links between the segments are shown in accordance with the findings of Goppel and Knotnerus.<sup>8</sup> We suspect that these ester groups arise from the rearrangement of peroxide links which formed originally through the coupling of free radicals produced by the reaction with oxygen.

The cracked tar asphaltene of Figure 8 is related to the natural asphaltene of Figure 6 and can be made from it by aromatizing portions of the ring system of Figure 6 and by breaking off aliphatic fragments from the natural asphaltene. These processes are known to occur in cracking of petroleum hydrocarbons.

A few hypothetical structures for asphaltenes have been presented in the literature. None of these is entirely consistent with the proton magnetic resonance data reported in this paper. The asphaltene drawn in a previous paper by Winniford<sup>3</sup> contains too much benzylic hydrogen and not enough methyl hydrogen. That drawn by Carlson, et al,<sup>14</sup> is much too low in methylene hydrogen and also has too much benzylic and not enough methyl. The structure drawn by Gardner, Hardman, Jones, and Williams<sup>2</sup> for their petroleum Fraction No. 10 is a near asphaltene in chemical composition; but its loose structure contains far too much aromatic hydrogen for an asphaltene and probably, therefore, it should be drawn as a more compactly condensed molecule. The structure drawn by Given<sup>15</sup> for bituminous coals cannot be correct for petroleum asphaltenes as it contains far too much oxygen and shows no methyl or methylene hydrogen at all.

The chemical nature of asphaltenes can by no means be considered settled by the brief results of this study. It is not believed that large deviations from

these results on the ratios of various classes of hydrogen will be found. However, more information is needed on the nature of links between the ring systems and on the size of the ring systems. Also, the disposition of the heterocyclic atoms, oxygen, sulfur, and nitrogen should be further clarified.

#### Acknowledgment

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TABLE I  
ANALYTICAL DATA ON ASPHALTENES

	Asphaltene			
	Venezuelan	Californian	Air-Blown Californian	Cracked Californian
<u>Per Cent</u>				
Carbon	81.17	85.54	86.22	88.43
Hydrogen	7.86	8.08	8.22	6.63
Nitrogen	2.02	3.33	2.0	2.08
Sulfur	6.89	1.28	1.89	2.24
Oxygen	2.02	2.48	3.74	0.62
Carbon/Hydrogen Ratio	0.86	0.89	0.88	1.12

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TABLE II

RATIOS OF THE AMOUNTS OF METHYLENIC,  
METHYL, BENZYLIC, AND AROMATIC PROTONS  
SHOWN BY THE PMR SPECTRA

	Venezuelan	Californian	Air Blown Californian	Cracked Californian
Methylene	1.00	1.00	1.00	1.00
Methyl	0.39	0.60	0.90	0.49
Benzyllic	0.29	0.45	0.44	0.72
Aromatic	Trace	0.19	0.16	0.66

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FIG. 1  
ASPHALTENE FROM VENEZUELAN  
CRUDE OIL

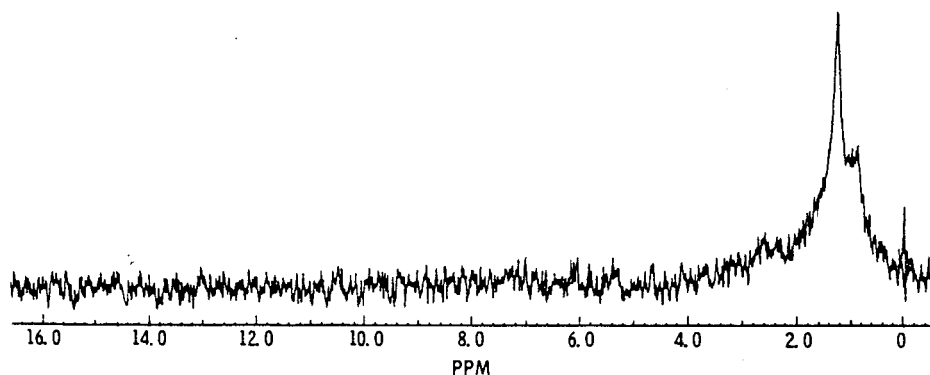
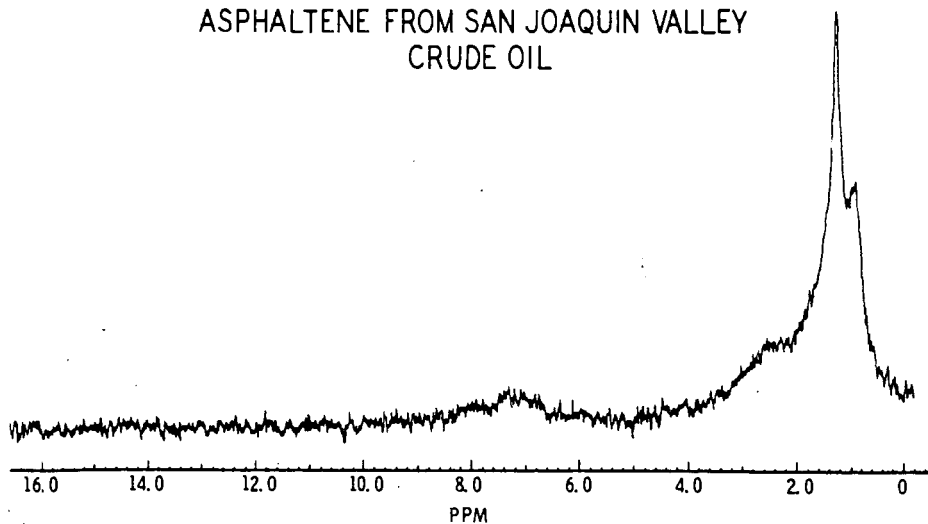


FIG. 2  
ASPHALTENE FROM SAN JOAQUIN VALLEY  
CRUDE OIL



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FIG. 3  
ASPHALTENE FROM AIRBLOWN  
SAN JOAQUIN VALLEY RESIDUUM

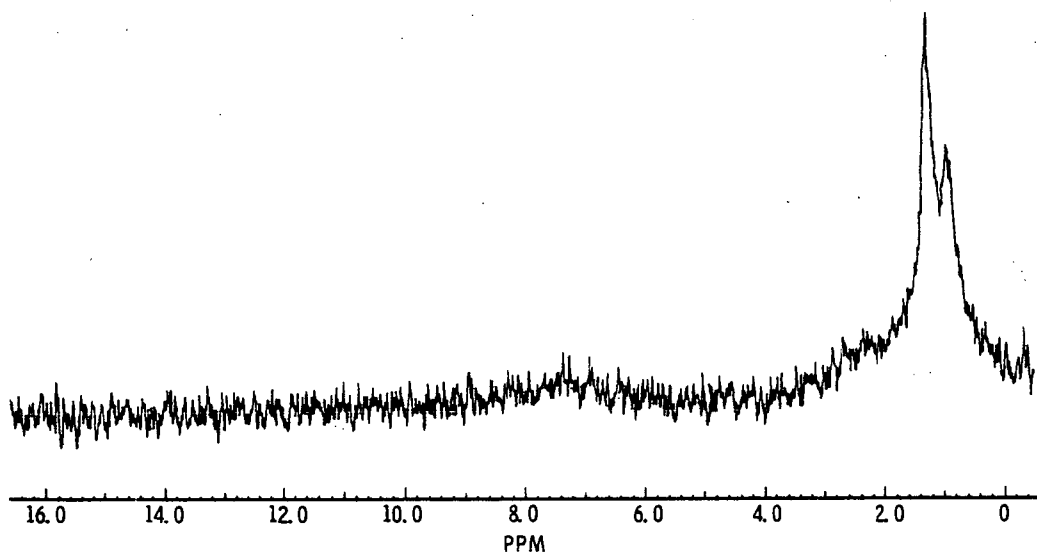
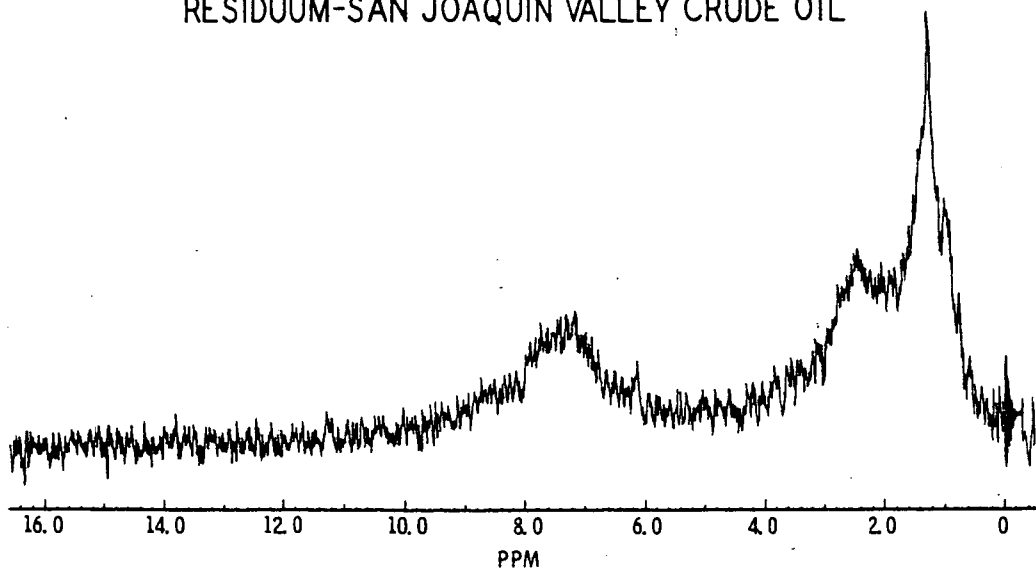


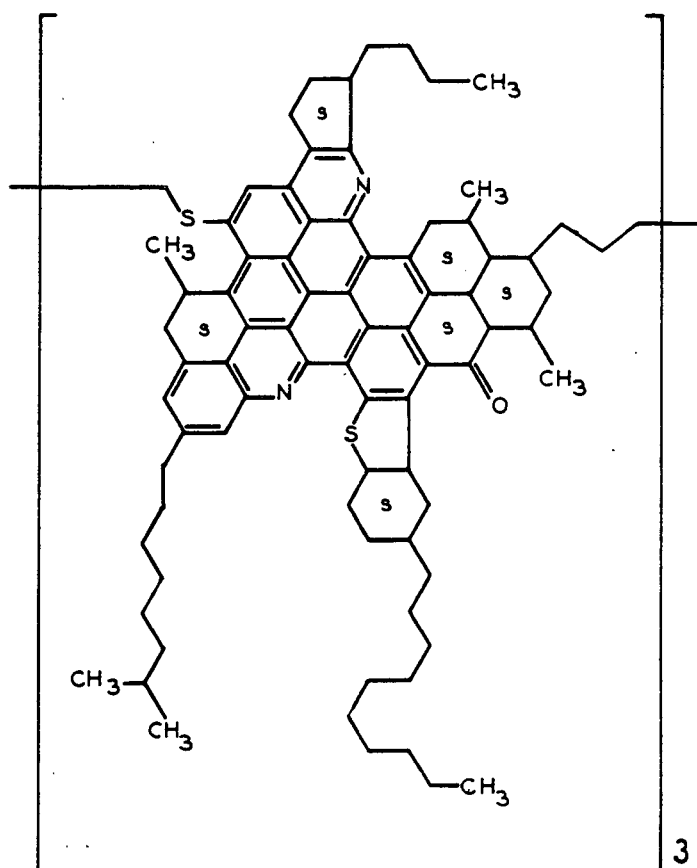
FIG. 4  
ASPHALTENE FROM THERMALLY CRACKED  
RESIDUUM-SAN JOAQUIN VALLEY CRUDE OIL



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FIG. 5  
 ASPHALTENE FROM VENEZUELAN  
 CRUDE OIL



$(C_{79}H_{92}N_2S_2O)_3$   
 Mol Wt 3449

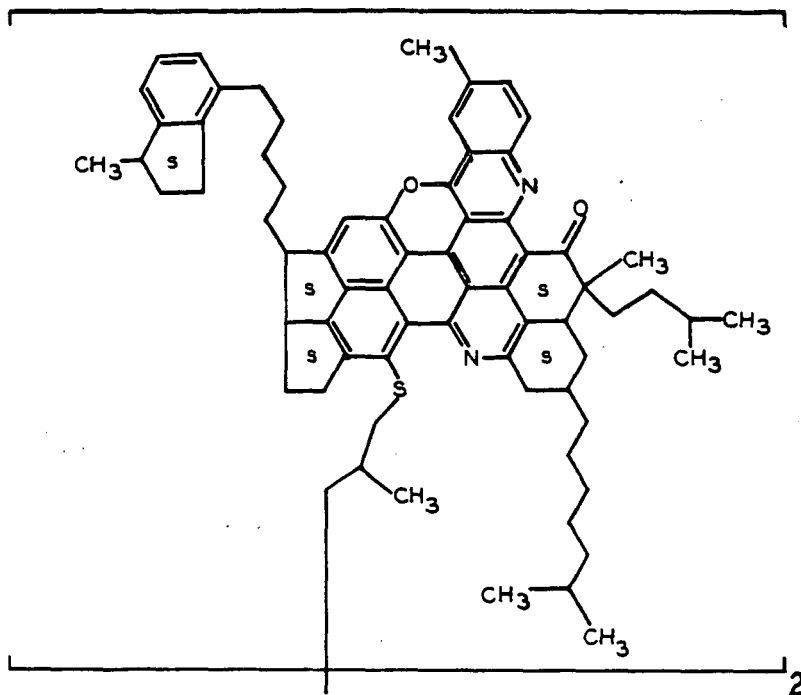
#### Hydrogen Distribution

Ratios	
Methylene	1.00
Methyl	0.40
Benzyllic	0.28
Aromatic	0.06

#### Composition

% C =	82.5
% H =	8.0
% N =	2.5
% O =	1.4
% S =	5.6
C/H Ratio =	0.86

FIG. 6  
 ASPHALTENE FROM SAN JOAQUIN  
 VALLEY CRUDE OIL



(C<sub>70</sub>H<sub>79</sub>N<sub>2</sub>O<sub>2</sub>S)<sub>2</sub>  
 Mol Weight 2024

Hydrogen Distribution  
 Ratios

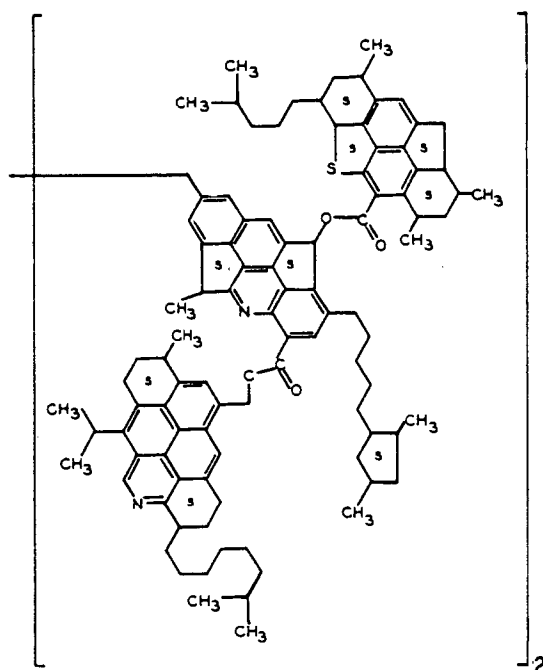
Methyl	0.58
Methylene	1.00
Benzylic	0.42
Aromatic	0.19

Composition

% C =	83.0
% H =	7.8
% N =	2.8
% O =	3.2
% S =	3.2
C/H Ratio =	0.89

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FIG. 7  
 ASPHALTENE FROM AIRBLOWN SAN JOAQUIN  
 VALLEY RESIDUUM



$(C_{98}H_{113}N_2O_4S)_2$   
 Mol Weight 2830

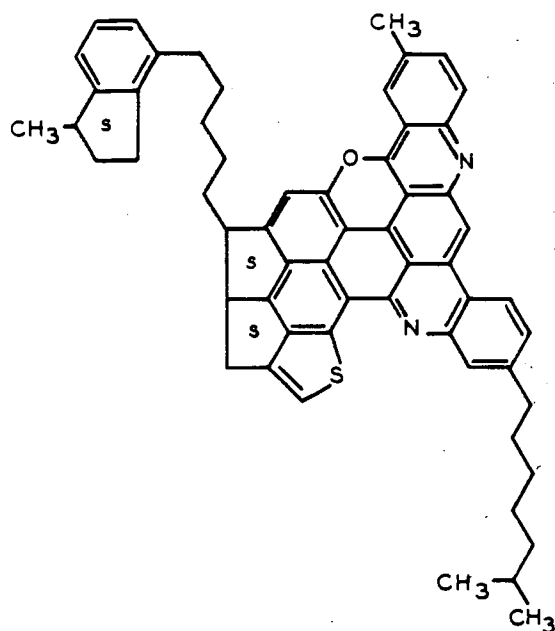
#### Hydrogen Distribution

Ratios	
Methylene	1.00
Methyl	0.89
Benzylic	0.47
Aromatic	0.18

#### Composition

% C =	83.1
% H =	8.1
% N =	2.0
% O =	4.5
% S =	2.3
C/H Ratio =	0.87

FIG. 8  
 ASPHALTENE FROM THERMALLY  
 CRACKED RESIDUUM-SAN JOAQUIN VALLEY  
 CRUDE OIL



$C_{59}H_{54}N_2SO$   
 Mol Wt 838

Hydrogen Distribution  
 Ratios

Methylene	1.00
Methyl	0.47
Benzyllic	0.74
Aromatic	0.63

Composition

% C =	84.5
% H =	6.4
% N =	3.3
% S =	3.8
% O =	1.9
C/H Ratio =	1.09